

of 600 km to the source, total bremsstrahlung production efficiency of 13% (27), 30 photons detected for an average TGF, and an instrumental effective area of 250 cm², we require $\sim 3 \times 10^{15}$ 35-MeV electrons, for a total energy of ~ 20 kJ or a power of ~ 40 MW over 0.5 ms. Beaming would make these numbers lower, even as it made the inferred number of TGFs higher. Although thin-target bremsstrahlung gives a better fit, the electron content in the thin-target case is unconstrained and could be much higher. For upward-beamed electrons, ignoring Earth's magnetic field, the transition between thin and thick target would take place at ~ 30 km.

TGFs near geomagnetic latitude 45° have been considered as a source of ~ 1 -MeV electrons in Earth's inner radiation belt by Lehtinen *et al.* (17). Inner-belt electrons above 10 MeV are more relevant to our results and were detected by Mariya-2 on the Mir station (28). The RHESSI TGFs, however, have an average geomagnetic latitude of 14°, and for these the electrons would be tied to magnetic field lines that skim the atmosphere and could not become trapped. As we analyze the whole RHESSI data set—almost 3 years and counting—we will either measure or place limits on high-latitude TGFs that may contribute to the inner-belt electrons above 10 MeV.

We are searching with a number of groups for coincidences between RHESSI TGFs and different kinds of lightning and TLEs. With TGFs for the whole RHESSI mission, we will compare these populations statistically as well.

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Materials and Methods
References and Notes

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Iron Isotope Constraints on the Archean and Paleoproterozoic Ocean Redox State

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The response of the ocean redox state to the rise of atmospheric oxygen about 2.3 billion years ago (Ga) is a matter of controversy. Here we provide iron isotope evidence that the change in the ocean iron cycle occurred at the same time as the change in the atmospheric redox state. Variable and negative iron isotope values in pyrites older than about 2.3 Ga suggest that an iron-rich global ocean was strongly affected by the deposition of iron oxides. Between 2.3 and 1.8 Ga, positive iron isotope values of pyrite likely reflect an increase in the precipitation of iron sulfides relative to iron oxides in a redox stratified ocean.

The rise of atmospheric oxygen, which began by about 2.3 Ga (1–3), was one of the most important changes in Earth's history. Because Fe, along with C and S, are linked to and maintain the redox state of the surface environment, the concentration and isotopic composition of Fe in seawater were likely affected by the

change in the redox state of the atmosphere. The rise of atmospheric oxygen should have also led to dramatic changes in the ocean Fe cycle because of the high reactivity of Fe with oxygen. However, deposition of banded iron formations (BIFs) during the Paleoproterozoic era suggests that the deep ocean remained anoxic, at least episodically, until about 1.8 Ga, which allowed high concentrations of Fe(II) to accumulate in the deep waters (4).

Here we use Fe isotope systematics (5) to provide constraints on the redox state of the Archean and Paleoproterozoic oceans and to identify direct links between the oxidation of the atmosphere and the Fe ocean cycle.

Laboratory and field studies suggest that Fe isotope variations are associated mainly with redox changes (6, 7). Lithogenic sources of Fe on the modern oxygenated Earth, such as weathering products, continental sediments, river loads, and marine sediments, have isotopic compositions similar to those of igneous rocks (8, 9). In contrast, seafloor hydrothermal sulfides and secondary Fe-bearing minerals from the altered oceanic crust span nearly the entire measured range of $\delta^{56}\text{Fe}$ values (5) on Earth, from -2.1 to 1.3 per mil (‰) (10, 11). Large variations of $\delta^{56}\text{Fe}$ (from -2.5 to 1.0 ‰) in Late Archean to Early Paleoproterozoic BIFs have been also reported (12), which highlight the roles of ferrous Fe oxidation, fluid-mineral isotope fractionation, and potentially microbial processes in the fractionation of Fe isotopes.

Study of S isotope composition of sedimentary pyrite over geological time has placed important constraints on the S cycle and the evolution of ocean chemistry (13). Here we apply a similar time-record approach in order to explore potential changes in Fe isotope compositions. Pyrite formation in modern organic-rich marine sediments is mediated by sulfate-reducing bacteria and proceeds essentially through the dissolution and reduction of lithogenic Fe oxides and Fe silicates to Fe(II), either below the sediment-water interface or in stratified euxinic bottom waters (14–16). During reduction of Fe oxides, diagenetic fluids with isotopically light Fe(II) may be produced (17, 18). However, the Fe

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isotope composition of sedimentary pyrite from Phanerozoic organic-rich sediments studied so far (Fig. 1 and table S2) (19) suggests that such processes are unlikely to produce sedimentary pyrite with $\delta^{56}\text{Fe} < -0.5\text{‰}$. It is presumed that most of reactive Fe is scavenged to form pyrite, minimizing Fe isotope fractionation regardless of the isotope effect during Fe reduction (17) and precipitation (20). In contrast, when high concentrations of Fe(II) accumulate under anoxic conditions and low sulfide concentrations, large $\delta^{56}\text{Fe}$ variations (10–12) may occur because of partial Fe(II) oxidation, Fe(III) reduction, and distillation processes during mineral precipitation. We thus hypothesize that Fe isotope variations in sedimentary pyrite are particularly sensitive to the concentration of dissolved Fe(II) and can be used to place important constraints on the sources and sinks of the Fe(II) reservoir.

We analyzed Fe isotope composition of sulfides in black shales ranging in age from Precambrian to Late Cretaceous, specifically focusing on Late Archean to early Paleoproterozoic time (Fig. 1) (21). The emerged general pattern of Fe isotope variations suggests that Earth's history may be divided into three stages, which are strikingly similar to the stages defined by multiple sulfur isotope and carbon isotope records, as well as other indicators of the redox state of the atmosphere and ocean (2, 3, 13, 22).

Stage I extends from before 2.8 Ga to about 2.3 Ga and is characterized by highly variable and negative $\delta^{56}\text{Fe}$ values. The range of $\delta^{56}\text{Fe}$ values between 0.5 and -3.5‰ is often observed within a single section of black shales, but individual pyrite nodules from the same stratigraphic level have similar $\delta^{56}\text{Fe}$ values (Fig. 2). Because dissimilatory Fe(III) reduction has been suggested to be important on early Earth (23) and is known to produce large Fe isotope fractionations (6, 24), it can be hypothesized that these extreme Fe isotope fractionations were produced by this metabolic activity. However, three independent observations argue against this hypothesis. First, Fe isotope fractionation during single-step bacterial reduction of Fe oxides (with an initial $\delta^{56}\text{Fe}$ value of 0‰) is unlikely to produce Fe(II) with $\delta^{56}\text{Fe}$ less than -1.3‰ (17). Second, if a $\delta^{56}\text{Fe}$ value as low as -3.5‰ can be generated through multiple steps of Fe oxidation and reduction, then the evidence for these processes should be evident in younger sediments, but they are not documented (Fig. 1). In addition, bacterial Fe(III) reduction is expected to produce pyrite with locally highly variable negative $\delta^{56}\text{Fe}$ values, depending on the extent of Fe(III) reduction and Fe(II) reoxidation. Our samples (Fig. 2 and table S2) do not show great variability between individual sulfide nodules and suggest a common source of Fe(II). Third, the amount of biogenically produced Fe(II) would need to be unrealistically high

during the Archean to swamp the global influence of hydrothermally derived Fe(II) with $\delta^{56}\text{Fe}$ values between 0 and -0.5‰ (8) delivered to the deep ocean.

Values of $\delta^{56}\text{Fe}$ as low as -2.3‰ have been observed in Fe-rich groundwater springs that precipitate isotopically heavy ferrihydrite along a fluid-flow path (25) and yield low $\delta^{56}\text{Fe}$ values in a residual Fe(II) pool. Adsorption of Fe(II) onto Fe oxide particles may

also provide an additional means to produce an isotopically negative Fe(II) pool through the preferential sorption of ^{56}Fe onto Fe oxide surfaces (24). In a similar manner, low $\delta^{56}\text{Fe}$ values for Archean oceans may reflect preferential sequestration of ^{56}Fe on Fe oxides (26, 27). Indeed, magnetite and hematite in BIFs are often characterized by positive $\delta^{56}\text{Fe}$ values (12), for example, $\delta^{56}\text{Fe}$ values up to 1.6‰ in iron formations of the ~ 2.7 Ga

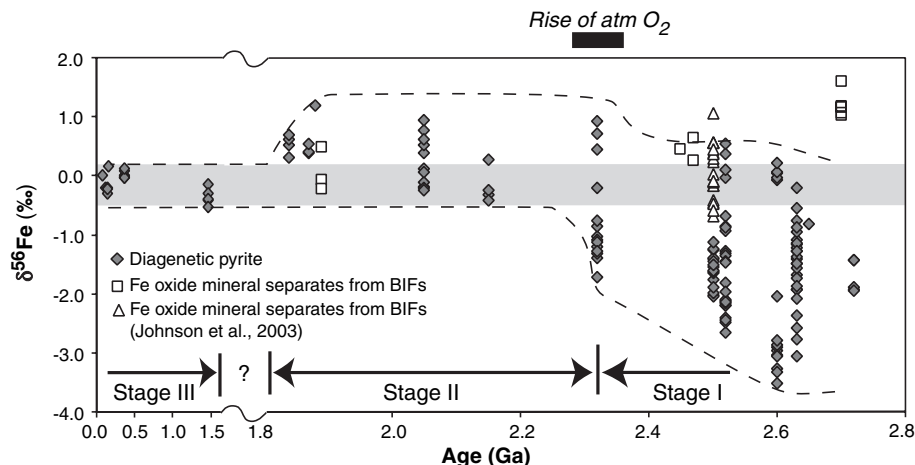


Fig. 1. Plot of $\delta^{56}\text{Fe}$ values versus sample age for Fe sulfides from black shales and Fe oxides from BIFs. On the basis of the $\delta^{56}\text{Fe}$ values, the Fe ocean cycle can be roughly divided into three stages: (i) stage I is from >2.8 to 2.3 Ga, (ii) stage II is from 2.3 to 1.8 Ga, and (iii) stage III is less than 1.7 Ga. Note the scale change between 1.5 to 1.8 Ga. The gray diamonds correspond to Fe isotope composition of pyrite from black shales (table S2), and open squares and triangles correspond to Fe isotope composition of magnetite- and hematite-rich samples from BIFs [table S3 and (12), respectively]. The gray area corresponds to $\delta^{56}\text{Fe}$ values of Fe derived from igneous rocks (at 0.1‰) and hydrothermal sources (about -0.5‰) (8). Dashed lines represent the contour lines of maximum and minimum Fe isotope compositions of sedimentary sulfides used to define Stages I to III. The rise of atmospheric oxygen (atm O_2) is defined by multiple sulfur isotope analyses of pyrite in the same samples as analyzed for Fe isotopes (3).

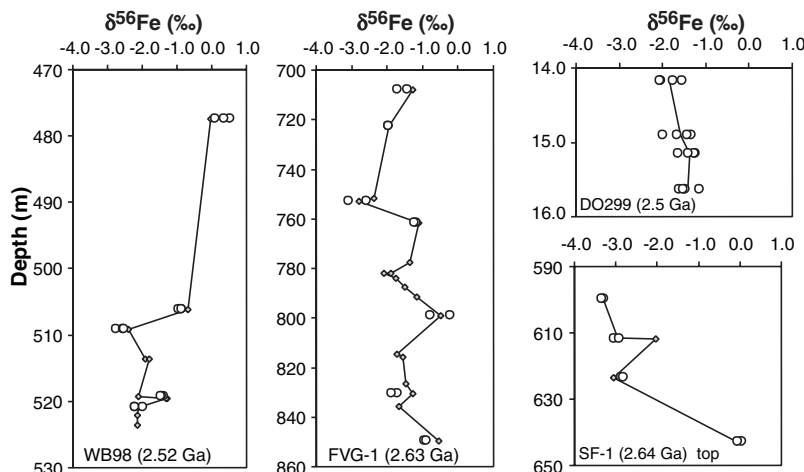


Fig. 2. Fe isotope composition of pyrite plotted along stratigraphic sections of black shales. $\delta^{56}\text{Fe}$ values of individual diagenetic pyrite nodules and pyrite grains (open circles) are plotted together with bulk pyrite values (gray diamonds) to illustrate possible Fe isotope heterogeneity within samples. Samples were selected from drill cores WB98 (Gamohaan Formation, Campbellrand Subgroup, Griqualand West Basin, South Africa, about 2.52 Ga); FVG-1 (Roy Hill Member of the Jeerinah Formation, upper part of the Fortescue Group, Hamersley Basin, Western Australia, about 2.63 Ga); DO299 (Mount McRae Shale, Mount Whaleback Mine, Newman, Hamersley Basin, Western Australia, about 2.5 Ga); and SF-1 (Lokammona Formation, Schmidtsdrift Group, Griqualand West Basin, South Africa, about 2.64 Ga).

Belingwe Belt, Zimbabwe (Fig. 1). Large stratigraphic variations in $\delta^{56}\text{Fe}$ of sedimentary pyrites in ~ 2.7 - to ~ 2.5 -Ga black shales, up to 3‰ over tens to hundreds meters of section (Fig. 2), suggest changes in Fe isotope composition of seawater over short periods of time on the order of a few million years. This implies a nonsteady state of the Archean Fe cycle with variable Fe concentrations caused by the competitive effect of Fe oxide precipitation and Fe supply from hydrothermal sources. These rapid changes of Fe concentrations are consistent with the idea that Fe oxide deposition in BIFs resulted from the episodic upwelling of Fe-rich deep waters accompanied by partial biological and/or abiological oxidation (26) in shallow waters (28). Alternatively, Fe oxide deposition within marine sediments on continental shelves or in the deep ocean may have also provided an important sink for Fe between periods of large BIF deposition.

We used a simple Rayleigh distillation model to explore the influence of Fe oxide deposition on the Fe isotope composition of seawater (29). Fe is delivered to the ocean from rivers and from seafloor hydrothermal systems with $\delta^{56}\text{Fe}$ values ranging from 0.0 to -0.5‰ (8). Fe is then removed by precipitation of Fe oxides. $\delta^{56}\text{Fe}$ values as low as -3.5‰ are only reached when more than 90% of the Fe from the initial Fe pool is precipitated as Fe oxides. $\delta^{56}\text{Fe}$ values of -1.5 to -2.0‰ , which are more typical of Late Archean sulfides, correspond to about 50% of the Fe precipitated as oxides. This value is similar to the estimates of Fe sink in BIFs based on P adsorption (30).

Stage II, which covers the time interval from about 2.3 to about 1.7 Ga, is characterized by the disappearance of negative $\delta^{56}\text{Fe}$ values and the emergence of positive $\delta^{56}\text{Fe}$ values up to 1.2‰. Major perturbations in biogeochemical and climatic record occurred during the beginning of stage II. These include the following: (i) negative and positive carbon isotope excursions in carbonates sandwiched between glacial diamictites, (ii) Earth's earliest global glaciations, and (iii) oxidation of Earth's atmosphere as suggested by increasing seawater sulfate content inferred from the $\delta^{34}\text{S}$ record and appearance of sulfate evaporites; disappearance of nonmass-dependent S isotope fractionation; appearance of red beds, oxidized paleosols, hematitic oolites, and pisolites; Mn oxide deposits; and Ce anomalies in chemical sedimentary deposits (3, 13, 22, 31). The appearance of positive $\delta^{56}\text{Fe}$ values, which persisted until about 1.7 Ga, together with the disappearance of strongly negative $\delta^{56}\text{Fe}$ values, occurred during the period when the most sensitive indicators for the rise of atmospheric oxygen first appeared. All these observations suggest that the oxidation of the surface environment in the early Paleoproterozoic was relatively rapid and that it directly affected the Fe isotope composition of the ocean.

How the change in the Fe isotope record about 2.3 Ga corresponds with change of the oceanic Fe cycle and the redox state of the ocean is not straightforward. Large BIF deposits are almost entirely lacking between 2.3 and 2.1 Ga (32), which is consistent with the lack of negative $\delta^{56}\text{Fe}$ values during this period. However, BIF deposition returned at about 2.1 Ga, and major BIFs were deposited in North America and Australia (32). If $\delta^{56}\text{Fe}$ values of pyrites in black shales that were deposited between 2.1 and 1.8 Ga are representative of the whole ocean, then BIF deposition mechanisms were different from those prevailing during the Archean. We infer that late Paleoproterozoic BIFs were deposited in an oxygenated layer of the ocean, and complete precipitation of Fe from Fe-rich plumes upwelling from the deep ocean did not affect the Fe isotope composition of the deep ocean. Despite the limited number of analyses, the narrow range of $\delta^{56}\text{Fe}$ values of hematite and magnetite from the 1.88-Ga Biwabik and Tyler formations compared with Archean BIFs (Fig. 1 and table S3) is consistent with this assumption.

An important consequence of the rise of atmospheric oxygen levels was the initiation of oxidative weathering and an increase in sulfate delivery to seawater (13). Consequently, the formation of Fe sulfides in the water column of pericratonic basins may have become the dominant part of the global ocean Fe cycle and may have prevented deposition of large BIFs, except during periods of intense submarine volcanic activity followed by high hydrothermal input of Fe. The effect of the increased role of sulfide production on the Fe isotope record is presently uncertain because reliable estimates of equilibrium Fe isotope fractionation during pyrite formation are lacking (20). One plausible hypothesis is that the positive $\delta^{56}\text{Fe}$ values in 2.3 to 1.8 Ga sedimentary sulfides might be related to sulfide precipitation from an Fe-rich pool with $\delta^{56}\text{Fe}$ composition around 0‰ and a pyrite-Fe(II) fractionation factor of up to 1‰ as suggested in previous studies (10, 33). This hypothesis indicates that sulfide produced by sulfate-reducing bacteria during this period has been completely titrated by dissolved Fe species in the Fe-rich and sulfide-poor ocean.

The disappearance of major BIFs after about 1.8 Ga is thought to indicate that the deep ocean became either progressively oxic or euxinic (4). Because the solubility of Fe sulfides and Fe oxides was low, most of the hydrothermally derived Fe(II) was likely rapidly precipitated in the deep ocean, allowing few possibilities to produce Fe isotope fractionation. The lack of substantial $\delta^{56}\text{Fe}$ value variations in sulfides from black shales younger than 1.5 Ga is thus consistent with the general picture that the whole ocean was Fe-poor after about 1.6 Ga. But the lack of variation does not place constraints on the

oxic versus sulfidic nature of the deep ocean. More data that cover the Phanerozoic, Mesoproterozoic, and Neoproterozoic time intervals are required to understand fully the change in the ocean Fe cycle at about 1.8 Ga.

Our Fe isotope record provides new insights into the Archean and Paleoproterozoic ocean chemistry and redox state. Fe isotopes suggest that the Archean oceans were globally Fe rich and that their Fe isotope composition and Fe content were variable in response to the episodic establishment of an Fe-rich pool supplied by hydrothermal activity and the deposition of Fe oxides, either in BIFs or dispersed throughout sediments on continental shelves and in the deep sea. After the rise of atmospheric oxygen by about 2.3 Ga, the Paleoproterozoic ocean became stratified and characterized by an increase of sulfide precipitation relative to Fe oxide precipitation. During this period, BIFs were likely deposited by upwelling of Fe(II)-rich plumes and rapid oxidation in the oxygenated layer of the ocean. Conducting Fe isotope analyses of sedimentary sulfides in conjunction with S isotope analyses should enable a more refined understanding of the origin of the positive Fe isotope excursion and the biogeochemical cycles of Fe and S during the Paleoproterozoic era.

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 21. Samples from different black shale units of similar ages were selected to distinguish between local and global effects on Fe isotope composition of seawater. We extracted between 10 and 20 sulfide grains to obtain a best estimate for the average $\delta^{56}\text{Fe}$ value for each sample. For comparison and to evaluate heterogeneity, we also analyzed several individual sulfide nodules from the same samples (table S2).
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 27. A magnetite-Fe(II) fractionation factor of about 2.4‰ has been inferred from BIFs data (12), which is slightly less than the equilibrium Fe(III)-Fe(II) fractionation factor of 2.9‰ at 22°C (42). The fractionation between ferrihydrite and Fe(II) of 1.5‰ measured during anaerobic photosynthetic Fe(II) oxidation by bacteria (43) is slightly larger than the 0.9‰ fractionation measured during abiotic oxidation of Fe(II) to ferrihydrite (25).
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$$\delta^{56}\text{Fe} = (1000 + d^{56}\text{Fe}_i) \times F^{(\alpha_{\text{BIF}} - 1)} - 1000$$
 where $\delta^{56}\text{Fe}_i$ is the initial value of hydrothermally derived Fe(II) at -0.5‰ (8) and α_{BIF} is the fractionation factor during Fe oxidation and Fe oxide precipitation, ranging between 1.0015 and 1.0023 (6).
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Materials and Methods

Fig. S1

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References

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Stem Lagomorpha and the Antiquity of Glires

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We describe several fossils referable to *Gomphos elkema* from deposits close to the Paleocene-Eocene boundary at Tsagan Khushu, Mongolia. *Gomphos* shares a suite of cranioskeletal characters with extant rabbits, hares, and pikas but retains a primitive dentition and jaw compared to its modern relatives. Phylogenetic analysis supports the position of *Gomphos* as a stem lagomorph and excludes Cretaceous taxa from the crown radiation of placental mammals. Our results support the hypothesis that rodents and lagomorphs radiated during the Cenozoic and diverged from other placental mammals close to the Cretaceous-Tertiary boundary.

Rodents and lagomorphs, collectively known as Glires, represent much of the modern diversity of mammals and have played an important role in understanding the timing of placental mammal diversification. On paleontological grounds, the origin of Glires is hypothesized to have taken place close to the Cretaceous-Tertiary boundary (1–3), a result compatible with some recent estimates from molecular studies (4,5). In contrast, other molecular estimates of Glires divergence have suggested a much older date, extending to 80

(6) or even more than 110 (7) million years ago (Ma). Paleontological support for an older date for Glires divergence has been proposed by studies supporting a close relationship between fossil zambdalestids and Glires (8–10). Zambdalestids are an extinct central Asian group of eutherian mammals (11, 12); their first appearance 85 to 90 Ma (10), coupled with a sister-taxon relationship with lagomorphs and/or rodents, would imply the presence of a Glires stem lineage more than 20 million years before the first appearance of any undis-

puted placental mammal. Until recently, stem lagomorphs (13, 14) were known from fragmentary craniodental remains (15), with few specimens associated with postcrania (16). Here we describe fossils of *Gomphos elkema*, including a specimen with an articulated skull and skeleton (Fig. 1), from the Nemegt Basin, Mongolia, and re-evaluate the origin of Glires.

G. elkema was first described as a paramyid-like rodent on the basis of lower-cheek teeth from deposits overlying Paleocene rocks at Gashato, Mongolia (17–19). The specimens discussed here are older and were recovered from a number of localities near Tsagan Khushu, Mongolia (19, 20), from the base of the Bumban Member of the Naran Bulak Formation, dating to the Paleocene-Eocene boundary (21). *Gomphos* has enlarged, gliriform

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